ABSTRACT

Molecular sieves are crystalline inorganic materials with framework density below twenty. Aluminophosphates (AlPO₄) are novel types of molecular sieves reported in early eighties by Union Carbide workers. Metal containing molecular sieves have been shown to be active redox catalysts. This thesis deals with two types of redox catalysts viz. (i) Titanium-aluminophosphate molecular sieves (TAPO₄) of AFI and AEL topologies and (ii) Zeolite-Y encapsulated metal-SALEN complexes (metal = Mn, Fe and V).

Before attempting TAPO₄ synthesis, AlPO₄ synthesis were standardised for the gel composition R : Al₂O₃ : P₂O₅ : 40H₂O, where R is triethylamine/tripropylamine for AlPO₄-5 and di-n-propylamine/di-n-butylamine for AlPO₄-11. TAPO₄-5 and TAPO₄-11 were synthesised without altering the AlPO₄ synthesis procedure, with x TiO₂ as titanyl peroxide (a titanium source), where x varied from zero to 0.125. Crystallisation of TAPO₄ were studied by changes observed in pH and titanium contents of formed crystal at various intervals for different temperatures. Relative crystallinity and kinetic parameters were calculated from pH profiles. Studies on titanium content indicate that there is greater chance for more AlPO₄ to grow over TAPO₄ at later stage of crystallisation, especially at high temperature. Copper and titanium substituted AlPO₄-s (CTAPO₄-s) were also synthesised.

The synthesised materials were identified by powder XRD and their unit cell constants were calculated. A decrease in unit cell constants were observed. Thermal analysis indicates that the materials were stable over a wide range of temperature and major amount of template leaves from as-synthesised samples around 550°C. DRS spectra revealed the presence of tetrahedral Ti(IV) in the framework. Laser-Raman spectra proved the absence of anatase in the materials. Calcined material shows IR shoulder at 1040 cm⁻¹, which was also observed for VAPO₄ and CrAPO₄. This peak was assigned to oxo species
vibrations. MAS-NMR studies indicate that Al and P are in tetrahedral environment. The surface area of calcined materials ranged from 100 to 250 m$^2$/g. SEM pictures show spherically agglomerated crystals with pure phase. Thermal studies, FT-IR analysis, chemical composition and $^{31}$P MAS-NMR indicate the presence of trace amount of template and P$_2$O$_5$ in the channels, which were responsible for the reduction in surface area.

Zeolite-Y encapsulated metal-SALEN complexes were prepared by ion-exchange, followed by complexation of SALEN ligand. The obtained materials were purified by soxhlet extraction using CHCl$_3$ followed by exchange by brine solution. TGA analysis indicates the presence of atleast one complex per supercage and also additional amounts of ligand. Encapsulation of metal complexes were further confirmed by UV-visible spectra, IR spectra, $^{13}$C MAS-NMR studies and ESR studies. From ESR analysis spin-Hamiltonian parameters were evaluated. The VO-SALEN complex showed lower symmetry in zeolite cage than it is in free form.

Hydroxylation of phenol with 30% hydrogenperoxide (1:3 molar ratio) in water as solvent gave catechol and hydroquinone over TAPO$_4$-s, CTAP$_4$-s and metal-SALEN-Y with overall conversion of 18-32, 30-32 and 26-28 wt% respectively. Oxidation of toluene was also carried out under similar conditions with acetone as solvent, which gave benaldehyde as major product with overall conversion ranging from 9 to 12 wt%. Further, the influence of oxidant concentration, time, solvent and temperature were studied for hydroxylation of phenol.

Structural refinement of TAPO$_4$-5 was also attempted in order to understand the unit cell reduction on substitution of titanium in the frame work.

In conclusion, through modified procedure anatase-free TAPO$_4$ were prepared, which were found to posses redox catalytic ability. Metal-SALEN-Y also were prepared and found to have equal redox capability as titanium molecular sieves.